

Recent Progress in water soluble Fluorescent sensors for detection of Al^{+3} , Fe^{+3} and Cu^{+2} ions

Dr. Deepa D Parab¹, Vishal O Yadav² & Dr. Harmeet Kaur Kohli^{3*}

^{1,2,3}Department of Chemistry, Guru Nanak Khalsa College of Arts, Science & Commerce (Autonomous), Mumbai-400019, Maharashtra, India. Corresponding Author Email: harmeet.kohli@gnkhalsa.edu.in*



DOI: <https://doi.org/10.38177/ajast.2025.9115>

Copyright © 2025 Dr. Deepa D Parab et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Article Received: 17 January 2025

Article Accepted: 18 March 2025

Article Published: 22 March 2025

ABSTRACT

A fluorescent sensor is a powerful technique used for detecting metal ions rapidly and effectively. It is a powerful tool for detecting metal ions in complex biological and environmental matrices. This review explores advancements in the development of water soluble fluorescence based sensors for metal ion detection focusing on Al^{+3} , Fe^{+2} and Cu^{+2} ions in aqueous medium. It explores the latest advancements in sensor design. Specifically, this review highlights the synthetic process, sensing mechanism, photophysical properties like detection limit, sensitivity, selectivity and performance of the water soluble sensors. By offering efficient, portable, and highly sensitive solutions, fluorescence sensors are poised to redefine metal ion detection across various fields. This review is expected to bring new clues and bright ideas to researchers for further advances in water soluble chemosensors in the future.

Keywords: Fluorescent sensors; Water soluble; Aluminum ion; Ferric ion; Copper ion; Fluorescence mechanism; Synthesis; Sensing mechanism; Phyto-physical properties; Detection limit; Sensitivity; Selectivity.

1. Introduction

Identifying metal ions is crucial for environmental monitoring and public health because of their widespread presence in nature, industrial processes, and biological systems. Metal ions, both essential and toxic, require precise monitoring to assess their impact and ensure safety. Among the various detection methods, fluorescence-based optical chemosensors have become increasingly significant for their sensitivity, selectivity, and real-time monitoring capabilities. These sensors operate by utilizing analyte-receptor interactions that trigger measurable photophysical changes, such as shifts in fluorescence, color variations, or changes in emission intensity, making them a practical and non-invasive option.

Extensive development has been devoted to fluorescent sensors for detecting a broad spectrum of species, including key metal ions such as Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Hg^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , and Al^{3+} . These ions are particularly significant because of their environmental and biological importance. Although traditional methods such as atomic absorption spectrometry and inductively coupled plasma mass spectrometry (ICP-MS) provide high accuracy, they are costly, involve complex instrumentation, and are impractical for on-site monitoring.

Despite their advantages, detecting metal ions in complex biological and environmental matrices, such as plant tissues, remains challenging. Interference from intrinsic fluorescence and secondary metabolites (e.g., tannins, alkaloids, and polyphenols) complicates the detection process. These probes leverage sophisticated photo-induced processes, including chelation-enhanced fluorescence, photo-induced electron transfer, intramolecular charge transfer, and aggregation-induced emission, enabling more reliable detection in intricate systems.

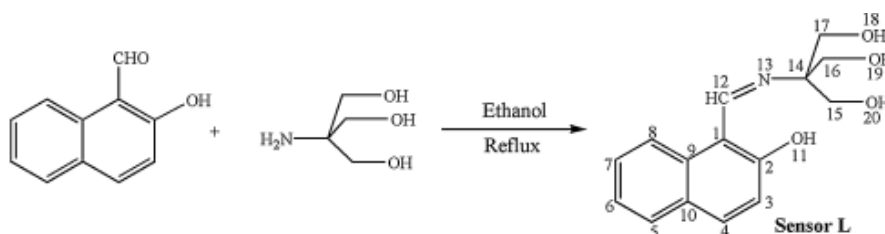
This review explores advancements in the development of fluorescence-based sensors for Al^{3+} , Fe^{+2} and Cu^{+2} ions.

1.1. Study Objectives

- (a) To help develop researchers provide a cost-effective, portable fluorescence sensor that supports real-time analysis, making them ideal for diverse applications.
- (b) To help researchers develop advanced fluorescent probes with improved specificity and sensitivity.
- (c) To help develop easy detection without requiring sophisticated instruments.
- (d) To help develop promising techniques allowing qualitative and quantitative detection of medically and environmentally important species without any sophisticated instrumentation.
- (e) To help design and synthesize fluorescent probes that can specifically bind to and detect target molecules.
- (f) To help study fluorescence properties of different materials to optimize their performance as sensors.
- (g) To help highly selectivity and sensitivity detection technique in terms of different color change for different species.

2. Water soluble fluorescent sensors for Al^{3+} ion detection

2.1. Naphthalene-based fluorophores have become pivotal in advancing fluorescent sensor development, particularly for metal ion detection. Researchers have concentrated on developing naphthalene derivatives incorporating water-soluble functional groups, maintaining compatibility with aqueous systems without sacrificing sensitivity or selectivity. Liu *et al.* [1] synthesized a novel Schiff-base fluorescent chemosensor, 2-Hydroxymethyl-2-[(2-hydroxy-naphthalen-1-ylmethylene) amino]-propane-1,3-diol (L) as shown in Scheme 2.1.



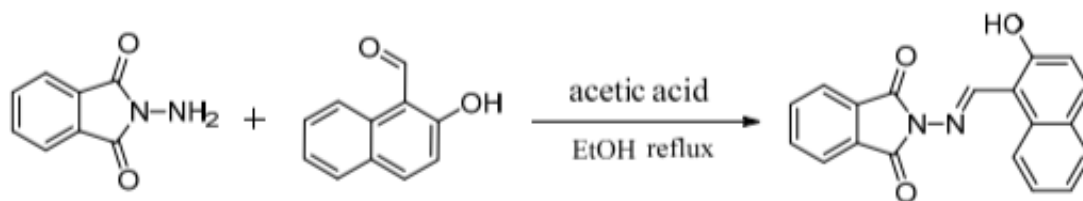
Scheme 2.1. Synthesis of 2-Hydroxymethyl-2-[(2-hydroxy-naphthalen-1-ylmethylene) amino]-propane-1,3-diol

This compound is produced through a condensation reaction between naphthol aldehyde and tris(hydroxymethyl) aminomethane (TRIS) in ethanol under reflux conditions, yielding a highly selective and water-soluble probe for Al^{3+} detection. The optical properties of sensor L were analyzed through UV-Vis and fluorescence spectroscopy, with a focus on its interaction with aluminum ions (Al^{3+}). In aqueous solution, L appears light yellow and displays a characteristic absorption band between 400–420 nm, attributed to the $n-\pi^*$ transition of the azomethine group. Upon the addition of Al^{3+} , the intensity of this band decreases, along with a reduction at 310 nm, indicating the formation of a 1:1 complex between L and Al^{3+} .

The fluorescence mechanism of L is governed by photoinduced electron transfer (PET). In the absence of Al^{3+} , the nitrogen atom in L donates its lone electron pair to the naphthyl ring fluorophore, leading to fluorescence quenching. However, when Al^{3+} binds to L, the PET process is inhibited, restoring fluorescence and producing a

strong blue emission under UV light. This fluorescence "switch-on" behavior is directly attributed to the interaction between L and Al^{3+} , which prevents electron transfer and activates light emission from the fluorophore. Titration experiments in water revealed that L demonstrates high sensitivity and selectivity for Al^{3+} at pH 7.0, with minimal interference from other metal ions. The detection limit for Al^{3+} was established at 1.0×10^{-7} M, confirming the sensor's ability to detect trace levels of aluminum ions.

2.2. Li, C.L *et al.* [2] synthesized a fluorescent sensor by condensing 2-hydroxy-1-naphthaldehyde and 2-aminoisindoline-1,3-dione (L) in dry ethanol, using acetic acid as a catalyst as shown in Scheme 2.2. The reaction was refluxed overnight and subsequently purified by solvent removal under reduced pressure.



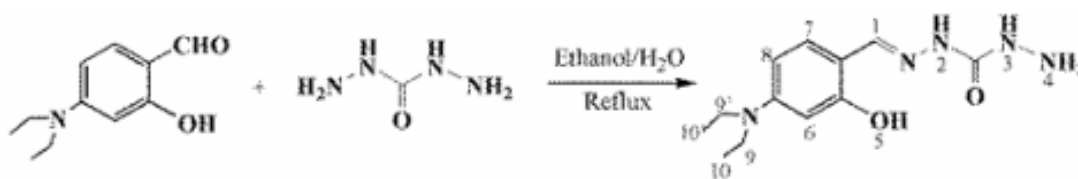
Scheme 2.2. Synthesis of Sensor L by condensing 2-hydroxy-1-naphthaldehyde and 2-aminoisindoline-1,3-dione (L) in dry ethanol

The design of the sensor allows it to selectively interact with Al^{3+} ions, leading to significant changes in its fluorescence and absorption spectra. In a DMSO- H_2O (1:9 v/v) solution, sensor shows absorption at 320 nm and 370 nm. When exposed to various metal ions, including Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Hg^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , and Al^{3+} , only Cu^{2+} and Al^{3+} resulted in noticeable spectral shifts.

Cu^{2+} induced a red shift in the absorption spectrum accompanied by a visible color change from dark green to black under UV light. Al^{3+} led to a reduction in absorption intensity, along with a color change from dark green to blue, also visible under UV light. Additionally, the presence of Al^{3+} significantly enhanced fluorescence intensity, producing a new emission band at 472 nm, which was 11 times stronger than the control.

The enhanced fluorescence upon Al^{3+} binding is attributed to the formation of a more rigid structure, confirmed by fluorescence titration, Job plot analysis, and ESI/MS results. Probe L forms a 1:1 complex with Al^{3+} , with an association constant of $3 \times 10^7 \text{ M}^{-1}$, indicating a strong interaction. The sensor proved effective for detecting Al^{3+} within a pH range of 5 to 10, making it well-suited for environmental applications with fluctuating pH levels. The probe effectively detected Al^{3+} in real-world water samples, exhibiting a distinct color change, thereby demonstrating its potential for monitoring aluminum contamination. To further expand its use, a paper-based detection method was developed by soaking filter paper in a DMSO- H_2O solution of probe L and allowing it to dry. When exposed to Al^{3+} paper exhibited a color change from dark green to light blue, offering a rapid, cost-effective, and simple detection method for on-site use.

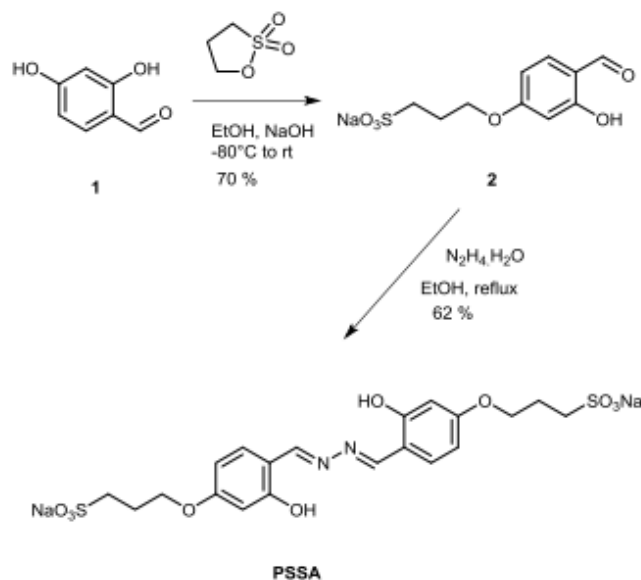
2.3. The development of β -cyclodextrin (β -CD) based fluorescent sensors present significant advancement in metal ion detection, particularly aluminum ions (Al^{3+}), in aqueous environments. Liu, Z.C. *et al.* [3] created the β -CD based sensor system by incorporating a fluorescent probe derived from diethylamine salicylaldehyde as shown in Scheme 2.3.



Scheme 2.3. Synthesis of 4-diethylaminobenzaldehyde carbohydrazide schiff-base

The sensor, synthesized through ultrasonic reactions, exhibits remarkable water solubility, selectivity, and sensitivity, making it a promising tool for both environmental and biological applications. In its unbound state, the sensor shows weak fluorescence, but the addition of Al^{3+} results in a 25-fold fluorescence enhancement, confirming its selective detection capabilities. Notably, the sensor is highly selective for Al^{3+} , with minimal interference from other metal ions, including Zn^{2+} , Cu^{2+} , and Fe^{3+} , as confirmed by fluorescence competition experiments. This selectivity is attributed to the coordination of Al^{3+} with specific oxygen and nitrogen atoms within the β -CD cavity. The sensor operates effectively under physiological conditions and is highly stable in pure water, outperforming other sensor systems tested in ethanol-water mixtures. It can detect Al^{3+} at concentrations as low as 10^{-7} M, with fluorescence intensity proportional to the metal ion concentration. Additionally, the sensor's performance is not influenced by the presence of EDTA, a strong chelator, indicating the irreversible nature of Al^{3+} coordination.

2.4. A novel fluorescent sensor, 4-propoxysulfonate salicylaldehyde azine (PSSA), designed by Nguyen *et al.* [4], for detection of aluminum (III) ion in aqueous solutions as shown in Scheme 2.4.

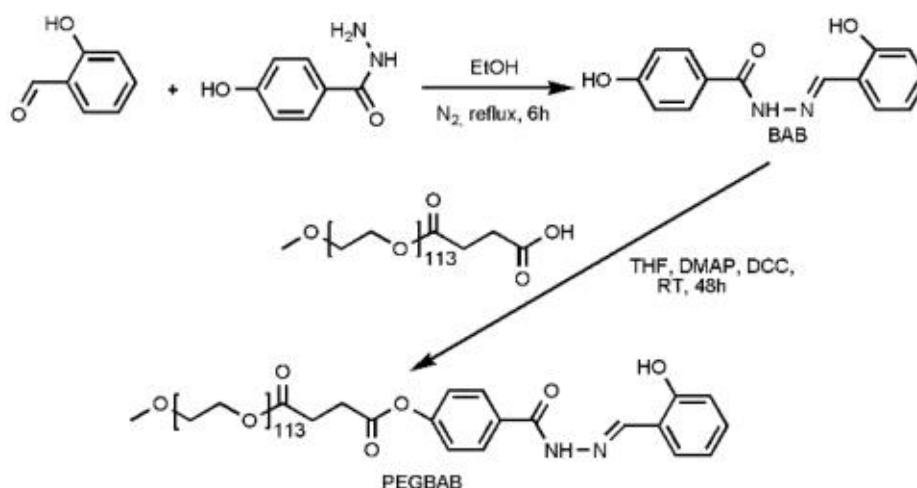


Scheme 2.4. Synthesis of PSSA ligand

PSSA's water solubility is enhanced by the incorporation of sulfonate functional groups, allowing for its direct use in environmental samples without the need for extensive preprocessing. The sensor demonstrates remarkable sensitivity, with detection limit of 153 nM, significantly lower than the World Health Organization's guideline for aluminum in drinking water. Additionally, PSSA shows excellent selectivity of aluminum(III), effectively distinguishing it from other metal ions such as Na(I), Mg(II), and Cd(II), making it reliable for complex environmental samples.

The sensor functions via an aggregation-induced emission enhancement (AIEE) mechanism, where aluminum(III) binding induces fluorescence enhancement through the formation of dendritic aggregates. PSSA was successfully integrated into a digital microfluidic platform, using a water-in-oil droplet approach, for portable, on-site detection of aluminum (III) ions.

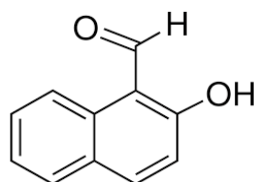
2.5. Bai, L *et al.* [5] designed PEGBAB, a novel water-soluble polymer engineered for the highly sensitive and selective detection of aluminum ions (Al^{3+}) in aqueous environment as shown in Scheme 2.5.



Scheme 2.5. Synthetic route of chemosensor PEGBAB

PEGBAB, which incorporates salicylidene Schiff base chemistry into a hydrophilic polyethylene glycol (PEG) polymer, demonstrates excellent fluorescence response to Al^{3+} with an impressive detection limit of 4.05×10^{-9} M, ensuring ultra-high sensitivity. The polymer shows exceptional selectivity for Al^{3+} , distinguishing it from Fe^{3+} , Cu^{2+} , and Zn^{2+} . It is stable across a wide pH range (2–13), with the best fluorescence response observed between pH 5 and 10. The system's fluorescence is also reversible in presence of ethylene diamine tetraacetic acid (EDTA), allowing for repeated use.

2.6. Liu *et al.* [6] used 2-Hydroxy-1-naphthaldehyde as a selective and sensitive fluorescent chemosensor for detecting Al^{3+} ions in ethanol-water solutions as shown in Scheme 2.6.

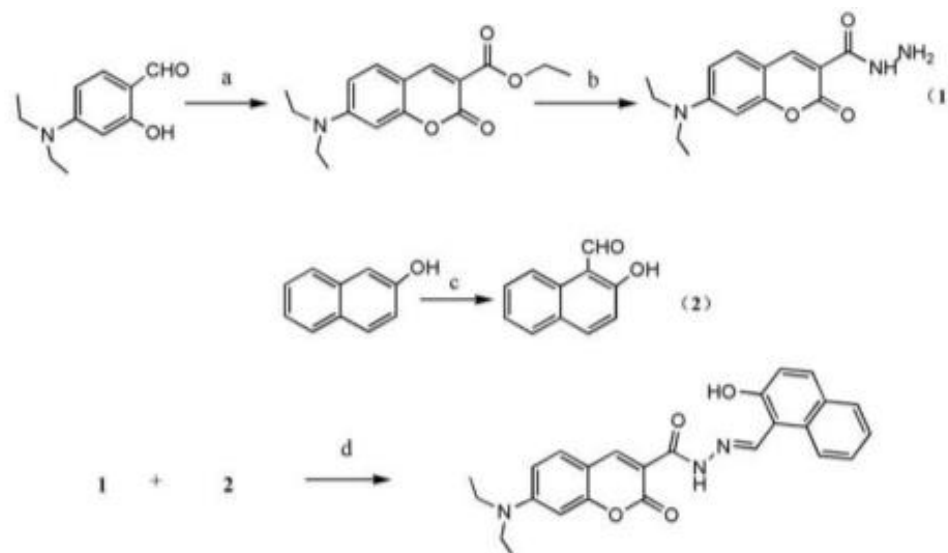


Scheme 2.6. Hydroxy-1-naphthaldehyde

Its salicyl functional group, which is activated by intramolecular hydrogen bonding, facilitates strong coordination with Al^{3+} , leading to chelation-enhanced fluorescence (CHEF). Among 15 tested metal ions, including Li^+ , Na^+ , K^+ , Ca^{2+} , Mn^{2+} , Hg^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , and Al^{3+} , the sensor exhibited a significant 12-fold fluorescence increase and a red shift from 435 nm to 445 nm when Al^{3+} was present. It showed no notable response to other ions or anions like CN^- , F^- , SO_4^{2-} , and SO_3^{2-} .

The sensor performed well across a pH range of 3–9 and maintained its selectivity for Al^{3+} even in mixtures with up to 40% water content, though the fluorescence intensity was halved compared to the optimal 95:5 ethanol-water ratio. The limit of detection for Al^{3+} was found to be 3.28×10^{-6} M, making it suitable for μM level detection in biological and environmental applications. Binding studies revealed a 1:1 stoichiometry between receptor 1 and Al^{3+} , supported by Job plot analysis, fluorescence titration, and mass spectrometry (m/z 219). ^1H NMR experiments showed that Al^{3+} binding disrupts the intramolecular hydrogen bonding within sensor, forming a rigid chelate structure.

2.7. Qin *et al.* [7] presented 7-diethylaminocoumarin-3-carbohydrazide as a fluorescent chemosensor as shown in Scheme 2.7 in having an innovative and efficient approach for the selective detection of Al^{3+} ions, leveraging a ratiometric fluorescence mechanism based on internal charge transfer (ICT) between coumarin and naphthalene moieties.

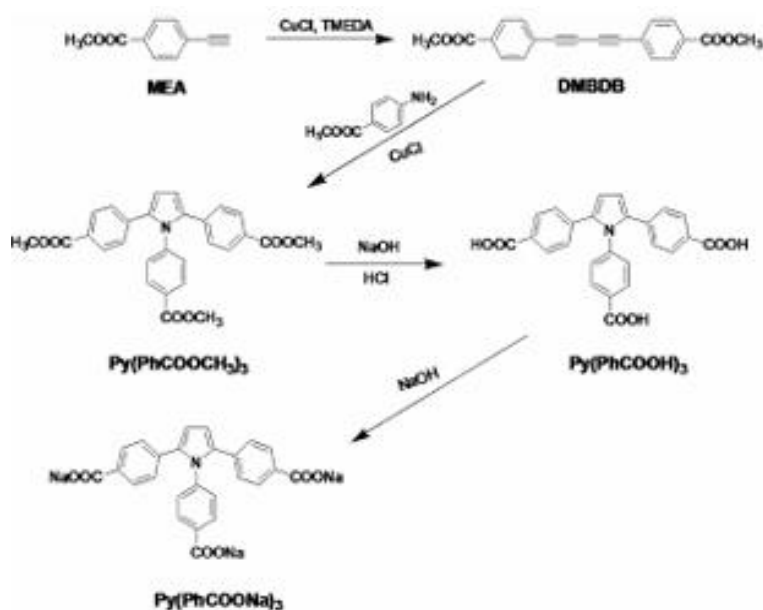


Scheme 2.7. 7-diethylaminocoumarin-3-carbohydrazide

In its free form, HL displays strong fluorescence at 481 nm in ethanol-water mixtures. However, upon interaction with Al^{3+} ions, the emission shifts significantly to 525 nm, signaling a disruption in the ICT process. This ratiometric change is attributed to the formation of a stable 1:1 complex between HL and Al^{3+} , which alters the sensor's photophysical properties. The sensor demonstrates exceptional selectivity for Al^{3+} over other common metal ions, including Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , making it highly reliable for use in complex environments where interference from other ions is a concern.

Extensive characterization through techniques such as UV-Vis, fluorescence titration, ESI-MS, and ^1H NMR spectroscopy confirms the 1:1 binding stoichiometry of HL and Al^{3+} . The detection limit of 3.3×10^{-6} M, well below the permissible Al^{3+} concentration in drinking water, demonstrates the sensor's sensitivity and effectiveness for real-time monitoring.

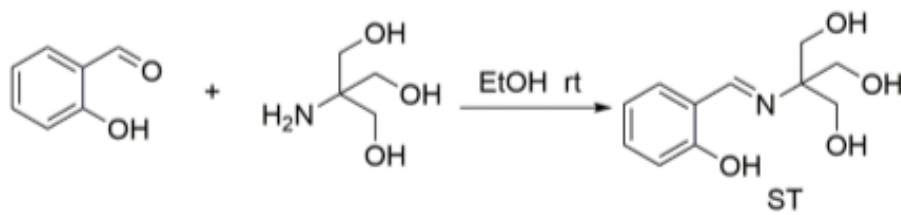
2.8. A novel water-soluble fluorescent sensor, sodium 4,4',4''-(1H-pyrrole-1,2,5-triyl)tri-benzoate ($\text{Py}(\text{PhCOO-Na})_3$), was designed by Shi, X *et al.* [8] to selectively detect aluminum ions (Al^{3+}) in aqueous solutions as shown in Scheme 2.8.



Scheme 2.8. Synthesis of $\text{Py}(\text{PhCOONa})_3$

The sensor displays aggregation-induced emission (AIE), where fluorescence intensity increases upon aggregation, functioning as a "turn-on" sensor for Al^{3+} with a fluorescence enhancement exceeding tenfold. Upon binding Al^{3+} , the sensor's emission undergoes a bathochromic shift, further enhancing its sensitivity. This sensor demonstrates exceptional selectivity for Al^{3+} over other metal ions, driven by the electrostatic interaction between Al^{3+} and the sensor's carboxylate groups, as well as the solubility differences of the resulting complexes. With a detection limit of $5 \mu\text{M}$ and a linear detection range of $5\text{--}120 \mu\text{M}$, it is well-suited for applications such as monitoring Al^{3+} in drinking water. The sensor's detection mechanism relies on the formation of a complex between Al^{3+} and its carboxylate groups, triggering the AIE process and causing a significant fluorescence increase. This process happens quickly, with the maximum fluorescence intensity reached within 10 seconds of introducing Al^{3+} , making it ideal for real-time detection. The high selectivity for Al^{3+} arises from its distinctive electrostatic binding interactions with the carboxylate groups and the solubility differences between the Al^{3+} sensor complex and those formed with other metal ions.

2.9. The newly developed water-soluble fluorescence sensor, 2-((2-hydroxybenzylidene)-amino)-2-(hydroxymethyl)propane-1,3-diol (ST), as shown in Scheme 2.9 by Liu, T *et al.* [9] offers a simple and cost-effective method for detecting aluminum ions (Al^{3+}) in aqueous solutions and on paper substrates.

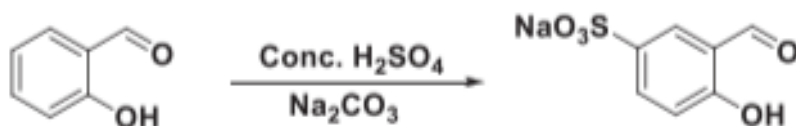


Scheme 2.9. Synthesis of 2-((2-hydroxybenzylidene)-amino)-2-(hydroxymethyl)propane-1,3-diol

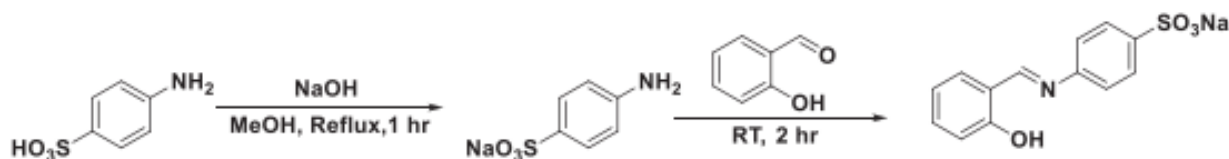
This Schiff-base compound was specifically designed for the selective detection of Al^{3+} , displaying a distinct "turn-on" fluorescence response upon interaction with the ion. ST effectively distinguishes Al^{3+} from other metal

ions, including In^{3+} , Ga^{3+} , Fe^{3+} , and Cr^{3+} , demonstrating high specificity. With a detection limit as low as 3.2×10^{-7} M, it is sensitive enough for detecting μM concentrations of Al^{3+} .

2.10. Ganesan, G *et al.* [10] synthesized sulfonated salicylaldehyde derivative (S1) and the π -conjugated sulfanilic acid analogue (SA1) for the selective detection of aluminum ions (Al^{3+}) as shown in Scheme 2.10.



Scheme 2.10a. Synthesis of sulfonated salicylaldehyde derivative (S1)



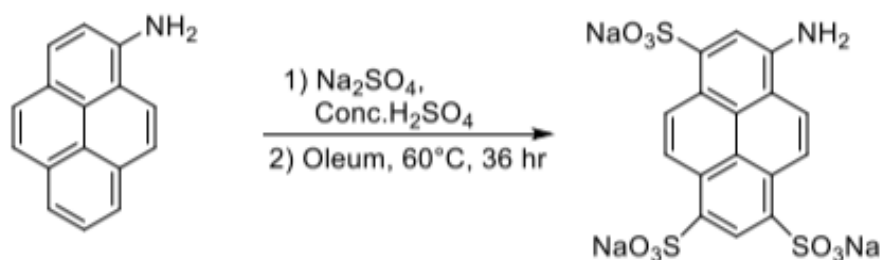
Scheme 2.10b. Synthesis of π -conjugated sulfanilic acid analogue (SA1)

These sensors are specifically engineered for water solubility, overcoming a common limitation of many organic conjugated scaffolds that are incompatible with aqueous environments. Photophysical studies of S1 and SA1 revealed exceptional selectivity for Al^{3+} , with little interference from other metal ions like Na^+ , Mg^{2+} , or Ca^{2+} . When exposed to Al^{3+} , both sensors exhibited substantial fluorescence enhancement, with emission maxima at 480 nm, attributed to the CHEF (Chelation Enhanced Fluorescence) mechanism.

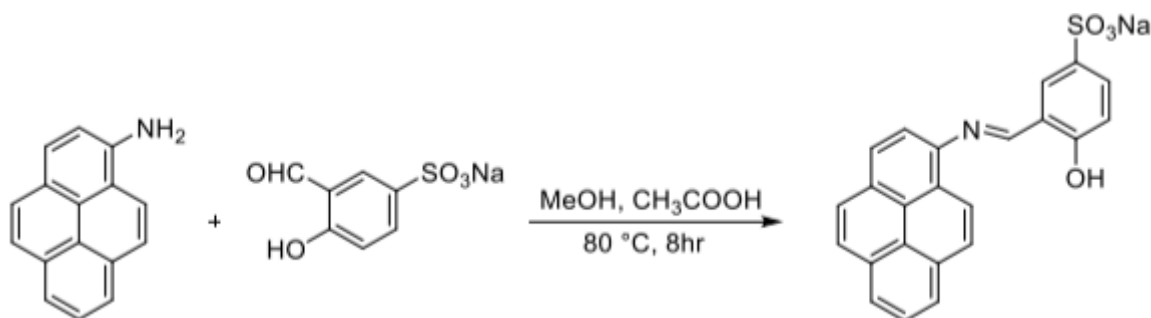
Quantitative analysis using Benesi-Hildebrand plots indicated strong binding constants ($K_b \approx 10^4$) and a 3:1 sensor-to-metal binding stoichiometry, which was confirmed by Electrospray Ionization Mass Spectrometry (ESI-MS). Notably, the detection limits for S1 (0.827 μM) and SA1 (1.67 μM) below the World Health Organization's permissible limits for aluminum in drinking water, making them highly suitable for environmental monitoring.

3. Water Soluble fluorescent sensors for Fe^{3+} ion detection

3.1. The development of two advanced fluorescent turn-off chemosensors, APTS (sodium 8-aminopyrene-1,3,6-trisulfonate) and APSS (sodium (E)-4-hydroxy-3-((pyren-1-ylimino)methyl)benzenesulfonate), as shown in Scheme 3.1a and 3.1b were designed by Chaskar, A *et al.* [11] for selective and sensitive detection of Fe^{3+} ions in aqueous environments.



Scheme 3.1a. Synthesis of APTS (sodium 8-aminopyrene-1,3,6-trisulfonate)

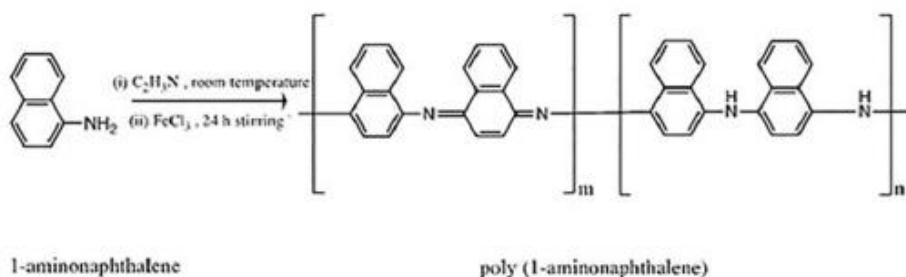


Scheme 3.1b. Synthesis of APSS (sodium (E)-4-hydroxy-3-((pyren-1-ylimino)methyl)benzenesulfonate)

These sensors exhibit remarkable performance, with detection limits of 45.6 nM for APTS and 45.9 nM for APSS, significantly lower than the Environmental Protection Agency's (EPA) guideline of 5.37 μM . The binding mechanisms of APTS and APSS with Fe^{3+} ions are confirmed through Job's plot and binding constant analysis, revealing a 2:1 stoichiometry for APTS and a 1:1 stoichiometry for APSS.

Both sensors are water-soluble due to their sulfonate groups, making them well-suited for detection in aqueous media. APTS, based on an aminopyrene structure, is prone to interference from Cu^{2+} ions, which can affect its performance. In contrast, APSS, incorporating a pyrene-based iminobenzene structure, demonstrates superior selectivity, unaffected by common interfering ions such as Cu^{2+} , Fe^{2+} , Al^{3+} , and Cr^{3+} . This makes APSS an excellent choice for real-time applications, including paper-strip-based detection. The binding constants further reveal that APTS has a binding constant of $2.69 \times 10^5 \text{ M}^{-1}$, while APSS shows a much higher binding constant of $4.06 \times 10^6 \text{ M}^{-1}$, indicating a stronger affinity for Fe^{3+} ions in APSS.

3.2. Nizar *et al.* [12] synthesized Poly(1-aminonaphthalene) (P1-AN) through chemical oxidative polymerization using FeCl_3 as a catalyst as shown in Scheme 3.2.



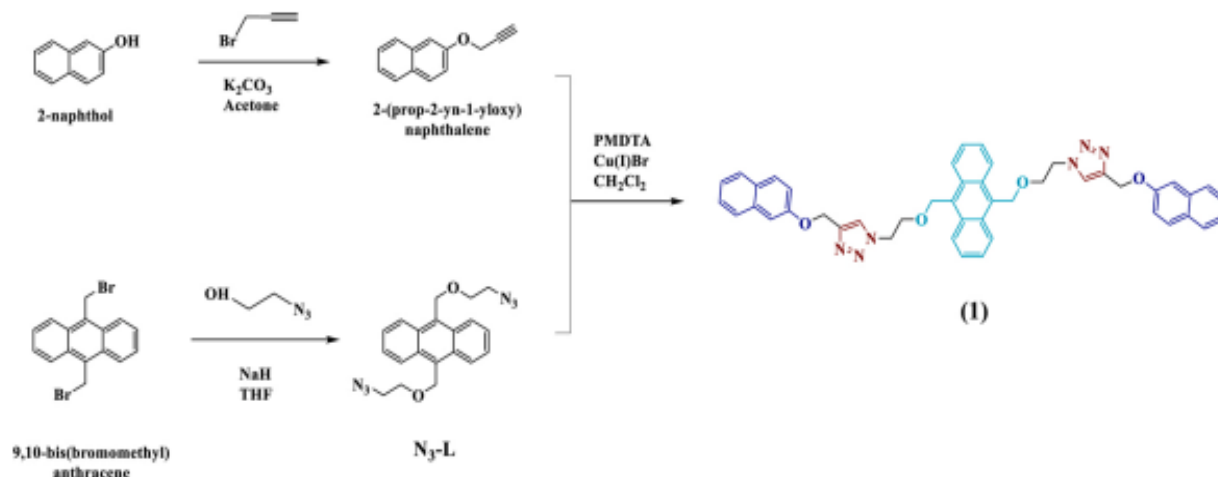
Scheme 3.2. Synthesis of P1-AN

Analysis through GPC and UV-Vis spectroscopy highlighted the polymer's conjugated structure, and it demonstrated excellent solubility in common organic solvents. These attributes position P1-AN as a promising material for practical applications, especially in aqueous environments.

The polymer exhibited remarkable chemosensing properties, particularly for detecting Fe^{3+} ions, via both colorimetric and fluorimetric methods. P1-AN exhibited excellent selectivity and sensitivity toward Fe^{3+} compared to other metal ions, with an immediate and visible color change from purple to yellow detectable by the naked eye. In fluorescence-based detection, it displayed a "turn-off" response, with significant quenching attributed to mechanisms such as electron transfer, hard acid interactions, and the paramagnetic nature of Fe^{3+} . The fluorescence

intensity showed a strong linear correlation with Fe^{3+} concentrations ranging from 10 to 50 mg/L, with a detection limit of 1.04 mg/L.

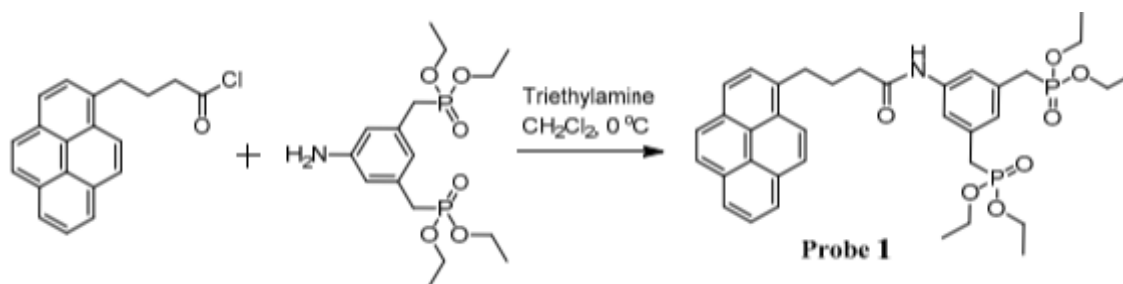
3.3. Tümay *et al.* [13] synthesized a novel dipodal fluorescence sensor, 9,10-bis((2-(4-((naphthalen-2-yloxy)methyl)-1H-1,2,3-triazol-1-yl)ethoxy)methyl) anthracene based on an anthracene platform for the selective detection of ferric ions (Fe^{3+}) as shown in Scheme 3.3.



Scheme 3.3. Synthesis of dipodal fluorescence sensor, 9,10-bis((2-(4-((naphthalen-2-yloxy)methyl)-1H-1,2,3-triazol-1-yl)ethoxy)methyl) anthracene

Photophysical analysis, including excitation-emission matrix (EEM) and 3D-fluorescence measurements, confirmed its robust fluorescent response. The sensor demonstrated high sensitivity and selectivity for Fe^{3+} , operating on a "turn-off" fluorescence mechanism, where the presence of Fe^{3+} induces fluorescence quenching. This enabled the detection of Fe^{3+} at low concentrations, with a limit of detection (LOD) of 0.314 μM and a linear detection range of 0.3–130 μM .

3.4. Padghan *et al.* [14] synthesized phosphate appended pyrene receptor in a single step via amide bond formation between pyrene butyric acid chloride and phosphonate-appended aniline as shown in Scheme 3.4.

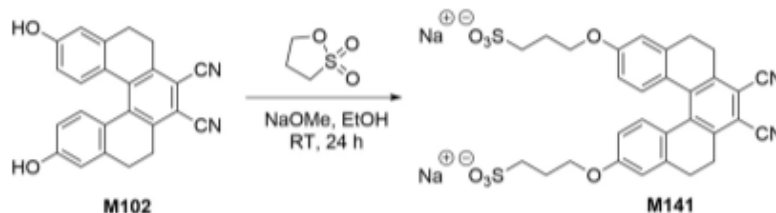


Scheme 3.4. Synthesis of phosphate appended pyrene receptor

A standout feature of receptor is aggregation-induced enhanced emission (AIEE) property, which is observed in water/acetonitrile mixtures with water fractions up to 80%. Dynamic light scattering (DLS) measurements show that these aggregates have an average size of around 142 nm, while field emission scanning electron microscopy (FE-SEM) reveals spherical aggregates formed upon solvent evaporation. These structural and photophysical characteristics make receptor 1 ideal for fluorescence-based sensing.

The Receptor demonstrates exceptional selectivity and sensitivity for Fe^{3+} ions, setting it apart from other metal ions. The detection mechanism relies on fluorescence quenching upon the formation of a 1:1 receptor- Fe^{3+} complex, which is confirmed by Job's plot analysis. This interaction induces significant spectral changes, making both UV-vis absorption and fluorescence emission spectroscopy viable detection methods. The reversibility of Fe^{3+} binding, shown by addition of EDTA, enhances its practicality for real-world use.

3.5 Petdum *et al.* [15] developed a novel Fe^{3+} fluorescence sensor, sodium 3,3'-((3,4-dicyano-1,2,5,6-tetrahydrodibenzo[c,g]phenanthrene-8,13-diyl)bis(oxy))bis(propane-1-sulfonate), M141, by combining a [5]helicene derivative with 1,3-propanesultone as shown in Scheme 3.5.



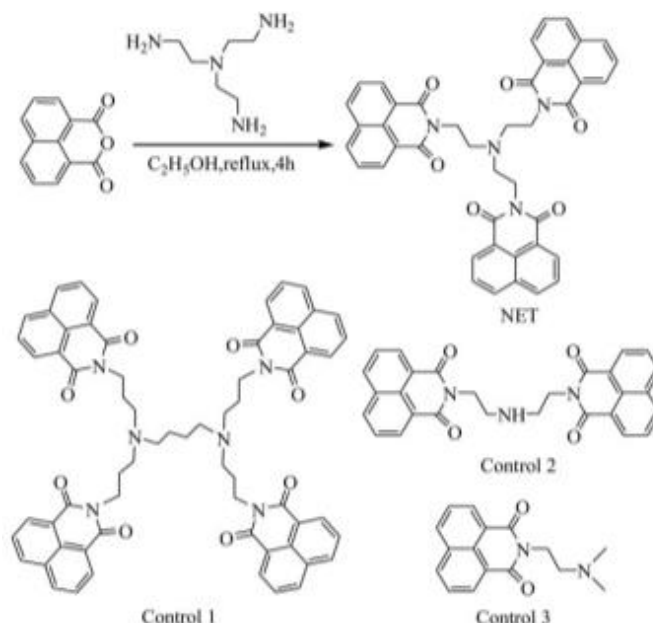
Scheme 3.5. Sodium 3,3'-((3,4-dicyano-1,2,5,6-tetrahydrodibenzo[c,g]phenanthrene-8,13-diyl)bis(oxy))bis(propane-1-sulfonate), M141

This sensor demonstrated highly sensitive fluorescence quenching specifically in presence of Fe^{3+} , with an exceptionally large stokes shift of 192 nm. This significant shift reduces spectral overlap, minimizing analytical errors during detection. M141 exhibited exceptional selectivity for Fe^{3+} over other metal ions in aqueous buffer solutions at physiological pH, making it a reliable tool for use in complex biological environments. Its water solubility enhances its compatibility with both biological and environmental applications. The sensor's limit of detection for Fe^{3+} was found to be 88 ppb (1.6 μM), which is much lower than the maximum permissible Fe^{3+} concentration in drinking water according to WHO and US EPA standards (0.3 ppm). Beyond controlled solutions, M141 was successfully applied for Fe^{3+} detection in human cancer cells. Furthermore, the sensor was incorporated into a flow injection analysis (FIA) system, enabling rapid and efficient Fe^{3+} quantification. The FIA method demonstrated a high throughput, processing up to 30 samples per hour, ideal for high-demand analytical scenarios.

3.6. A novel fluorescent dye, NET, composed of three 1,8-naphthalimide units connected to a nitrogen core (tris(2-aminoethyl)amine) was synthesized by Yang *et al.* [16] in a simple, one-step reaction under mild conditions as shown in Scheme 3.6.

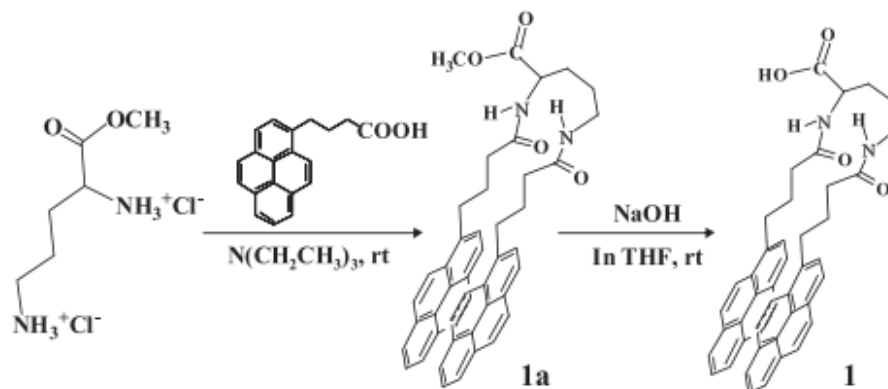
The fluorescence behavior of NET was studied in different organic solvents, specifically DMF (dimethylformamide) and DMF/ H_2O mixtures, revealing solvent-dependent fluorescence responses. In DMF, NET functions as a "turn-off" fluorescent sensor for Fe^{3+} ions, showing significant fluorescence quenching in presence of Fe^{3+} . However, in DMF/ H_2O mixtures, especially at 4:1 and 2:3 volume ratios, NET act as a "turn-on" sensor, exhibiting significant fluorescence enhancement in response to Fe^{3+} . This solvent-dependent behavior emphasizes the impact of the solvent environment on the fluorescence properties of NET, establishing it as a versatile tool for Fe^{3+} detection across different solvent systems. The study also delves into the binding characteristics of NET with Fe^{3+} , establishing a 1:1 stoichiometry of the complex, particularly in the DMF/ H_2O (2:3, v/v) mixture.

Spectroscopic techniques such as IR and ^1H NMR were employed to investigate the binding mechanism. NET demonstrated impressive selectivity and sensitivity toward Fe^{3+} ions, outperforming other similar sensors.



Scheme 3.6. Synthesis of three 1,8-naphthalimide units linked to a nitrogen core (NET) and structure of controls

3.7. An innovative fluorescent sensor N, N-bi[4(1-pyrene)-butyroyl]ornithine was designed by Zhao *et al.* [17] to detect and remove Fe^{3+} and Pb^{2+} ions from aqueous solutions as shown in Scheme 3.7.



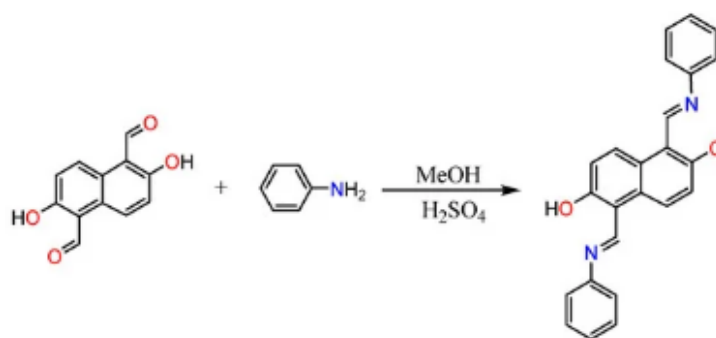
Scheme 3.7. Synthesis of sensor N, N-bi[4(1-pyrene)-butyroyl]ornithine

Unlike traditional applications of pyrene excimers as chromogenic units in ratiometric sensors, here they serve as hydrophobic units, promoting the formation of removable flocculent precipitates when coordinating with Fe^{3+} or Pb^{2+} . This coordination induces distinct fluorescence quenching, enabling efficient ion detection. The sensor demonstrates remarkable selectivity for Fe^{3+} in aqueous solutions containing 40% (v/v) acetonitrile, even in the presence of interfering metal ions. Furthermore, in solutions with 40% (v/v) dimethyl sulfoxide (DMSO), it exhibits similar sensitivity toward both Fe^{3+} and Pb^{2+} , highlighting its versatility across different solvents. Mechanistic studies reveal that the sensor's carboxyl group plays a pivotal role in binding Fe^{3+} and Pb^{2+} , forming highly hydrophobic complexes.

These hydrophobic complexes not only allow for precise ion detection but also facilitate practical removal from contaminated solutions, making the sensor an effective tool for environmental remediation. By combining detection with ion removal, this work broadens the utility of fluorescent sensors in environmental monitoring, analytical chemistry, and pollution control, offering a promising solution for addressing metal ion contamination.

4. Water soluble fluorescent sensors for Cu^{2+} ion detection

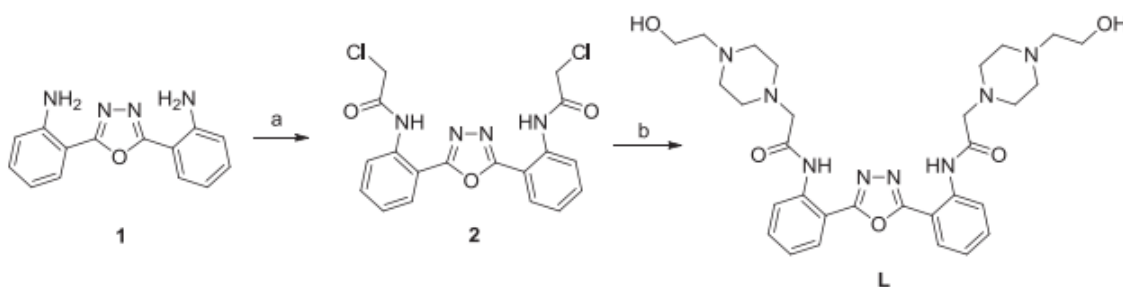
4.1. Zhang *et al.* [18] developed a novel Schiff base fluorescent probe, **probe L**, by functionalizing a naphthalene dialdehyde core with aniline as shown in Scheme 4.1, exhibited unique **aggregation-induced enhanced emission (AIEE)** properties. This simple, one-step condensation reaction yielded a precise and responsive probe for detection of **copper (II) ions (Cu^{2+})** in water.



Scheme 4.1. Synthesis of **probe** by functionalizing a naphthalene dialdehyde core with aniline

Interaction between the probe and Cu^{2+} ions resulted in a **fluorescence "turn-off" effect**, allowing for clear visual and instrumental detection. The threshold detection of the probe was found out to be exceptionally low, at $1.64 \times 10^{-8} \text{ mol L}^{-1}$, making it highly effective for trace-level Cu^{2+} detection. Spectroscopic studies, including UV-Vis and fluorescence titrations, were employed to explore the interaction mechanism between probe L and Cu^{2+} ions. The formation of 1:2 stoichiometric complex between probe L and Cu^{2+} was confirmed through Job's plot and $^1\text{H-NMR}$ titration experiments. The strong binding between the probe and Cu^{2+} ions was quantified, yielding a binding constant (K_a) of 1.222×10^5 , indicative of a robust and stable interaction. The "turn-off" behavior of probe L due to quenching effect induced by Cu^{2+} ions, because of their paramagnetic nature and their ability to interact with the π -conjugated system of the probe, disrupting its fluorescence.

4.2. Tang *et al.* [19] synthesized a novel hydrazine-derived Schiff base, 1-(8-methanylylidene-7-hydroxy-4-methyl-2H-chromen-2-one)-2-(2,4-dihydroxybenzylidene) hydrazine (abbreviated as L) as shown in Scheme 4.2.



Scheme 4.2. Synthesis of 1-(8-methanylylidene-7-hydroxy-4-methyl-2H-chromen-2-one)-2-(2,4-dihydroxybenzylidene) hydrazine, a; chloroacetic chloride and b; potassium iodide

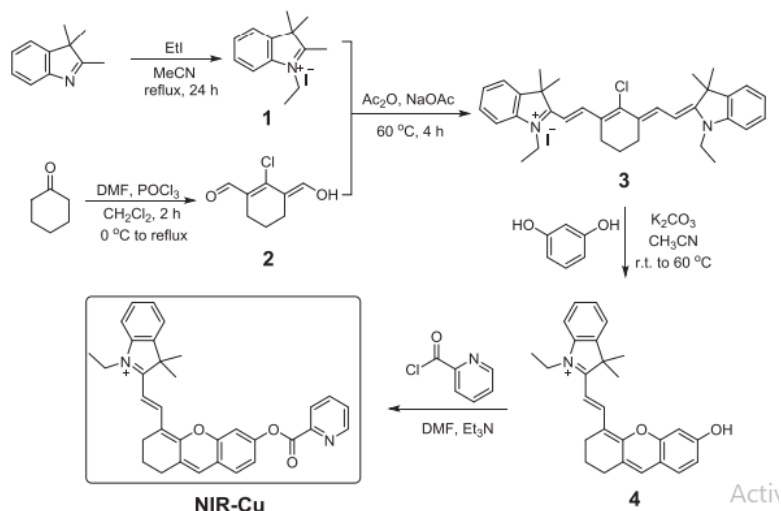
This compound exhibits a unique combination of colorimetric and fluorescence-based sensing capabilities, driven by its ESIPT (Excited-State Intramolecular Proton Transfer) properties. These characteristics make "L" an effective probe for detecting specific analytes in chemical contexts. The Schiff base "L" demonstrates a sensitive and selective response towards Cu^{2+} ions. The probe interacts with Cu^{2+} exhibits a noticeable color change from colorless to yellow, can be readily observed with the naked eye. This colorimetric response occurs with minimal interference from other common metal ions, confirming its selectivity. Such a capability makes "L" an efficient tool for detecting Cu^{2+} in complex mixtures.

Quantitative analysis using UV-Visible titration revealed a detection limit for Cu^{2+} of less than $30\ \mu\text{M}$. This value is significantly lower than the threshold recommended by the World Health Organization (WHO), emphasizing the probe's high sensitivity. Moreover, Competition studies confirmed that the presence of other metal ions caused minimal interference, further enhancing the reliability of the Schiff base for Cu^{2+} detection. The Schiff base "L" also exhibits remarkable fluorescence properties, particularly in an acetonitrile-water system. At higher water fractions (80% or more), "L" transitions into an aggregated state and displays Aggregation-Induced Enhanced Emission (AIEE). This behavior is attributed to the restriction of molecular motion in the aggregated state, which activates the ESIPT process.

Under these conditions, "L" emits a strong yellow fluorescence at 562 nm with a substantial Stokes shift of 205 nm, making it an excellent candidate for fluorescence-based detection systems. In pure acetonitrile, "L" displays a normal emission at 448 nm and an ESIPT emission at 549 nm, while the yellow fluorescence becomes prominent in the mixed acetonitrile-water system. The yield of the fluorescence emission was determined using quinine sulfate as a reference standard, further confirming the probe's efficiency.

A notable feature of the Schiff base "L" is its stability across a wide pH range of 4–7. Within this range, the fluorescence emission remains consistent, with no significant changes in intensity. This robustness ensures that the ESIPT process remains active in practical, environmentally relevant pH conditions.

4.3. Zhang *et al.* [20] developed a novel reaction-based fluorescent sensor, **NIR-Cu**, offering an exceptional platform for detection of Cu^{2+} ions as shown in Scheme 4.3.

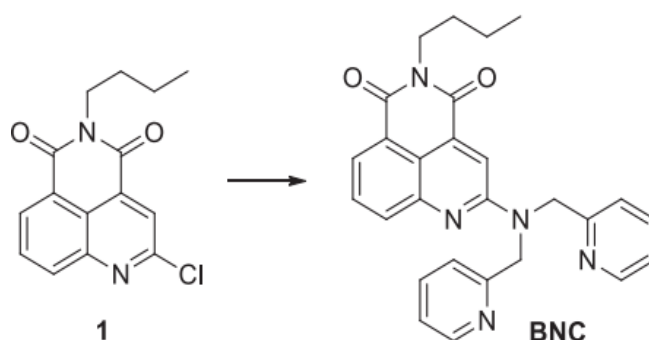


Scheme 4.3. Synthesis of reaction-based NIR excitation and emission probe, NIR-Cu

This sensor is distinguished by its near-infrared (NIR) excitation and emission capabilities, making it particularly well-suited for biological imaging applications. NIR-Cu is designed with an innovative functional group, 2-picolinic ester, which undergoes a specific hydrolysis reaction upon interaction with Cu^{2+} ions. This reaction induces a fluorescent "turn-on" response, exhibiting exceptional selectivity for Cu^{2+} over other metal ions, even in complex mixtures. Such specificity is crucial for precise metal ion recognition, particularly in biological and environmental settings where interference from competing ions is common.

The NIR-Cu sensor demonstrates a strong linear response to Cu^{2+} concentrations ranging from 0.1 to 5 μM . It achieves a remarkably low detection limit of 29 nM, significantly enhancing its utility for identifying trace amounts of Cu^{2+} in diverse samples. This level of sensitivity not only fulfills but exceeds the requirements for environmental and biomedical detection standards. Additionally, the sensor's excellent water solubility and rapid response time further solidify its applicability for real-time monitoring in aqueous systems.

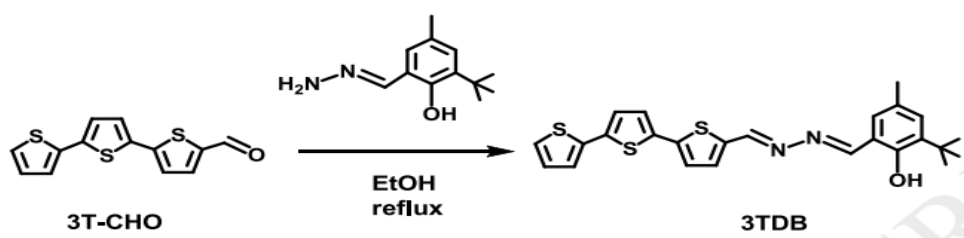
4.4. Zhang *et al.* [21] designed a novel 4,5-quinolimine-based fluorescent sensor, **BNC**, specifically designed for the selective and sequential detection of copper ions (Cu^{2+}) and cysteine (**Cys**) through fluorescence-based mechanisms as shown in Scheme 4.4.



Scheme 4.4. Synthesis of 4,5-quinolimine-based fluorescent sensor, BNC

The sensor showcases a unique "turn-off" fluorescence response to Cu^{2+} enabling sensitive detection with broad applicability in environmental, biological, and analytical contexts. **BNC** exhibits remarkable specificity for Cu^{2+} over a range of common metal ions. Upon binding to Cu^{2+} , the fluorescence of BNC is quenched, producing a clear "turn-off" signal. A **1:1 stoichiometric complex** forms between BNC and Cu^{2+} , stabilizing the interaction and facilitating the detection process. The detection limit (LOD) for Cu^{2+} was found to be 0.44 μM , showcasing the sensor's high sensitivity for trace-level detection.

4.5. Guo, Z *et al.* [22] designed a novel **oligothiophene derived colorimetric and fluorescent sensor, 3TDB** as shown in Scheme 4.5, for the highly selective, sensitive, and reversible detection of copper ions (Cu^{2+}).



Scheme 4.5. Synthesis of oligothiophene derived colorimetric and fluorescent sensor 3TDB

By combining visual and fluorescence-based detection, the sensor offers rapid and reliable Cu^{2+} sensing, with promising potential for applications in environmental monitoring, food safety, and biological studies. 3TDB undergoes a noticeable color shift from colorless to yellow in aqueous solutions upon binding with Cu^{2+} , enabling easy visual identification. Fluorescence of 3TDB is rapidly quenched ("turn-off" signal) when Cu^{2+} is present, providing a sensitive optical readout. 3TDB attains a low detection limit (LOD) of $0.42 \mu\text{M}$, enabling precise trace detection of Cu^{2+} . The sensor selectively detects Cu^{2+} , even amidst other competing metal ions, ensuring accuracy in complex matrices. The sensor exhibits a fast detection time, with fluorescence changes occurring within **20 seconds**, making it ideal for real-time analysis. 3TDB is effective over a wide pH range, enhancing its versatility for use in diverse environments. Job's plot confirmed that 3TDB forms a 1:1 stoichiometric complex with Cu^{2+} . The fluorescence quenching caused by Cu^{2+} can be reversed by adding EDTA, which removes Cu^{2+} from the 3TDB complex. This reversibility supports an **"ON-OFF-ON" fluorescence switch**, enabling controlled and repeatable detection cycles.

5. Conclusion

The research in designing fluorescent based sensors is expanding with great attention. The already known organic molecules provide advantage to the researchers to explore their binding affinity towards various metal ions. These sensors have been used for metal ion detection in common organic solvents, but their utility in aqueous media is not much explored. The review explores the wide scope to design water soluble fluorescent sensors by discussing the various synthetic process.

These sensors play an important role as simple, fast, economic, and efficient tools for detecting metal ions in complex biological and environmental matrices enhancing the practical applications. The sensing mechanism, emphasizes the coordination between the sensor and target ions by coordinating with atoms such as N, O, and S. Apart for sensitivity and selectivity, water solubility is the most significant property of these sensors, concerning the applications in environmental samples.

There is a space for developing new strategies for other metal ions as well in future. The development of Fluorescent sensors with high selectivity and sensitivity for harmful metal cations that can operate in a variety of media can be explored hereafter. New principles of sensors to discuss new possibilities of fluorescence-based sensors, can be described in coming times. Fluorescent sensors having application in studies of living systems, can be achieved by focusing on development of sensors-based detecting devices subsequently.

The review is intended to bring new ideas for further advances in water soluble fluorescent sensors.

Declarations

Source of Funding

This study did not receive any grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing Interests Statement

The authors declare no competing financial, professional, or personal interests.

Consent for publication

The authors declare that they consented to the publication of this study.

Authors' contributions

All the authors made an equal contribution in the Conception and design of the work, Data collection, Drafting the article, and Critical revision of the article. All the authors have read and approved the final copy of the manuscript.

Availability of data and material

Authors are willing to share data and material according to the relevant needs.

References

- [1] Liu, Zengchen, Li, Yanxia, Ding, Yongjie, et al. (2014). Water-soluble and highly selective fluorescent sensor from naphthol aldehyde-tris derivate for aluminum ion detection. *Sensors and Actuators B: Chemical*, 197: 200–205. <https://doi.org/10.1016/j.snb.2014.02.084>.
- [2] Chia-Lin Li, Ping-Hsuan Lu, Shih-Feng Fu, et al. (2019). A highly selective and sensitive fluorescent chemosensor for detecting Al^{3+} ion in aqueous solution and plant systems. *Sensors*, 19(3): 623. <https://doi.org/10.3390/s19030623>.
- [3] Liu Z.C., Zhu, W.P., Chen, Y.H., et al. (2015). Water-soluble host guest system from β -cyclodextrin as a fluorescent sensor for aluminium ions: synthesis and sensing studies. *Dalton Transactions*, 44(37): 16528–16533. <https://doi.org/10.1039/c5dt02220g>.
- [4] Nguyen, H.L., Kumar, N., Audibert, J.F., et al. (2019). Water-soluble aluminium fluorescent sensor based on aggregation-induced emission enhancement. *New Journal of Chemistry*, 43(38): 15302–15310. <https://doi.org/10.1039/c9nj03532j>.
- [5] Bai, L., Xu, Y., Li, G., Tian, S., Li, L., Tao, F., & Wang, L. (2019). A highly selective turn-on and reversible fluorescent chemosensor for Al^{3+} detection based on novel salicylidene Schiff base-terminated PEG in pure aqueous solution. *Polymers*, 11(4): 573. <https://doi.org/10.3390/polym11040573>.
- [6] Yen-Wen Liu, Chang-Hung Chen & An-Tai Wu (2012). A turn-on and reversible fluorescence sensor for Al^{3+} ion. *Analyst*, 137(22): 5201–5203. <https://doi.org/10.1039/c2an35854a>.
- [7] Qin, J.C., & Yang, Z.Y. (2015). Ratiometric fluorescent probe for Al^{3+} based on coumarin derivative in aqueous media. *Analytical Methods*, 7(5): 2036–2040. <https://doi.org/10.1039/c4ay02971b>.
- [8] Xiaoyan Shi, Huan Wang & Tianyu Han (2012). A highly sensitive, single selective, real-time and “turn-on” fluorescent sensor for Al^{3+} detection in aqueous media. *Journal of Materials Chemistry*, 22(36): 19296–19302. <https://doi.org/10.1039/c2jm33393g>.
- [9] Tianqi Liu, Xuejuan Wan, Yunsheng Dong, et al. (2017). Facile synthesis of a water-soluble fluorescence sensor for Al^{3+} in aqueous solution and on paper substrate. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 173: 625–629. <https://doi.org/10.1016/j.saa.2016.10.004>.

- [10] Ganesan, G., Pownthurai, B., Kotwal, N.K., et al. (2022). Function-oriented synthesis of fluorescent chemosensor for selective detection of Al^{3+} in neat aqueous solution: Paperstrip detection & DNA bio imaging. *Journal of Photochemistry and Photobiology A: Chemistry*, 425: 113699. <http://dx.doi.org/10.1016/j.jphotochem.2021.113699>.
- [11] Atul, C., Aniket, C.A., Omkar P., et al. (2023). A new water soluble, highly selective Pyrene-based fluorescent sensor for detection of Fe^{+3} metal ion. *Materials Chemistry*, 1: 1–19. <https://chemrxiv.org/engage/chemrxiv/article-details/64e3627300bbebf0e68c9e31>.
- [12] Nizar, S.A., Kobayashi, T., & Mohd Suah, F.B. (2020). An aminonaphthalene-based colorimetric and fluorescent sensor for selective recognition of Fe^{3+} in water. *Luminescence*, 35(8): 1286–1295. <https://doi.org/10.1002/bio.3890>.
- [13] Tümay, S.O., Irani-nezhad, M.H., & Khataee, A. (2020). Design of novel anthracene-based fluorescence sensor for sensitive and selective determination of iron in real samples. *Journal of Photochemistry and Photobiology A: Chemistry*, 402: 112819. <https://doi.org/10.1016/j.jphotochem.2020.112819>.
- [14] Sachin, D.P., Rajesh, S.B., Sidhanath, V.B., et al. (2017). Pyrene-phosphonate conjugate: aggregation-induced enhanced emission, and selective Fe^{3+} ions sensing properties. *Molecules*, 22(9): 1417. <https://doi.org/10.3390/molecules22091417>.
- [15] Petdum, A., Waraeksiri, N., Hanmeng, O., Jarutikorn, S., Chaneam, S., Sirirak, J., & Wanichacheva, N. (2020). A new water-soluble Fe^{3+} fluorescence sensor with a large Stokes shift based on [5] helicene derivative: Its application in flow injection analysis and biological systems. *Journal of Photochemistry and Photobiology A: Chemistry*, 401: 112769. <https://doi.org/10.1016/j.jphotochem.2020.112769>.
- [16] Liang Yang, Wen Yang, Dongmei Xu, et al. (2013). A highly selective and sensitive Fe^{3+} fluorescent sensor by assembling three 1, 8-naphthalimide fluorophores with a tris (aminoethylamine) ligand. *Dyes and Pigments*, 97(1): 168–174. <https://doi.org/10.1016/j.dyepig.2012.12.016>.
- [17] Zhao, M., Zhou, X., Tang, J., et al. (2017). Pyrene excimer-based fluorescent sensor for detection and removal of Fe^{3+} and Pb^{2+} from aqueous solutions. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 173: 235–240. <https://doi.org/10.1016/j.saa.2016.09.033>.
- [18] Zhang, X., Shen, L.Y., Zhang, Q.L., et al. (2021). A simple turn-off Schiff base fluorescent sensor for copper (II) ion and its application in water analysis. *Molecules*, 26(5): 1233. <https://doi.org/10.3390/molecules26051233>.
- [19] Tang, L., Zheng, Z., & Bian, Y. (2016). AN-(2-hydroxyethyl) piperazine dangled 2, 5-diphenyl-1, 3, 4-oxadiazole based fluorescent sensor for selective relay recognition of Cu^{2+} and sulfide in water. *Luminescence*, 31(8): 1456–1460. <https://doi.org/10.1002/bio.3128>.
- [20] Zhang, H., Feng, L., Jiang, Y., et al. (2017). A reaction-based near-infrared fluorescent sensor for Cu^{2+} detection in aqueous buffer and its application in living cells and tissues imaging. *Biosensors and Bioelectronics*, 94: 24–29. <https://doi.org/10.1016/j.bios.2017.02.037>.

- [21] Yu Zhang, Lan Li, Jinping Wan, et al. (2020). A 4, 5-quinolimide-based fluorescent sensor for sequential detection of Cu^{2+} and cysteine in water and living cells with application in a memorized device. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 230: 118030. <https://doi.org/10.1016/j.saa.2020.118030>.
- [22] Zongrang Guo, Tingting Hu, Xingjian Wang, et al. (2019). Highly sensitive and selective fluorescent sensor for visual detection of Cu^{2+} in water and food samples based on oligothiophene derivative. *Journal of Photochemistry and Photobiology A: Chemistry*, 371: 50–58. <http://dx.doi.org/10.1016/j.jphotochem.2018.10.053>.